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Sb–Cu–Li electrochromic mirrors

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Abstract

Switchable mirrors offer significant advantages over traditional electrochromic devices for control of incident light in architectural and aerospace applications due to their large dynamic ranges in both transmission and reflection in the visible and near infrared regimes. Here we describe construction and spectroscopic characterization of a complete electrochromic mirror device consisting of an antimony–copper alloy (40 at% Cu) active electrode coupled with an optically passive vanadium oxide counter electrode and a crosslinked polymer gel electrolyte. Transmittance and reflectance spectra in the visible–near IR (300–2500 nm) in both mirror and transparent states are reported. The photopic transmittance of the complete device varied from less than 3% to more than 20% during cycling, requiring about 40 min for complete switching in each direction. At the same time, the photopic reflectance varied from 40% to 25%. The crosslinked polymer improves the stability of the mirror electrode relative to that in a liquid electrolyte.
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Keywords: Electrochromism; Switchable mirrors; Thin films; Polymer electrolytes

1. Introduction

Switchable mirrors based on the interconversion of metallic antimony or bismuth and semiconducting phases via lithiation and delithiation of the host materials in a

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non-aqueous electrolyte were recently reported [1]. Potential applications include solar heat control for buildings, motor vehicles and airplanes, data switching, and display technologies. The charge required to switch an antimony mirror electrode, its electronic conductivity in the transparent state, and its optical properties were improved by the addition of copper or silver [2]. Because the commonly employed transparent conducting oxide coatings are unstable at the switching potentials, mirror electrodes prepared to date have relied upon the intrinsic conductivity of the active material. Volume expansion and contraction during cycling contribute to loss of connectivity within the electrode and eventually produce isolated regions that switch slowly or not at all. One approach to mitigate this effect is to use a rigid electrolyte, which tends to confine the volume changes to the electrode plane. Crosslinked polymer gel electrolytes have been shown to be compatible with electrochromic materials [3]. Here we describe construction of complete self-contained devices with superior cycling stability incorporating a vanadium oxide counter electrode and UV crosslinked gel electrolyte. The optical properties of the mirror electrode have also been measured over a wider spectral range than that previously reported.

2. Experimental

2.1. Electrode preparation and characterization

Sb–Cu alloy films 40 nm in thickness were deposited on 25 mm × 37 mm × 1 mm plain glass substrates by DC magnetron co-sputtering from separate 50 mm diameter targets angled 26° from normal, with target to substrate distances of 90 mm. The Sb:Cu mole ratio in the films was controlled at 3:2 by adjusting the sputtering power to the guns as determined from previous work [2]. Film thicknesses were measured by stylus profilometry (Dektak). Vanadium oxide films were prepared by spin coating 25 mm × 37 mm × 2.2 mm SnO_2:F-coated glass substrates with a vanadium oxyisopropoxide (Aldrich, Inc.) solution in isopropanol (10:3 volume ratio). The substrates were cleaned in a KOH/isopropanol base bath overnight and rinsed with deionized water. The coated substrates were dried at 100 °C for 2 h and then baked at 500 °C for 3 h in air to form a gray, amorphous V_2O_5 film 175 nm thick. Electrochemical cycling of individual Sb–Cu and V_2O_5 films was carried out in a helium-filled glove box with $O_2 < 1$ ppm and $H_2O < 2$ ppm in a 50 ml fused silica cuvette containing 1 M $LiPF_6$ in PC/EC (1:1), using lithium foil counter and reference electrodes. Upper and lower voltage limits were set at 1.2 and 0.7 V vs. Li^+/Li for the Sb–Cu films, and 4.0 and 1.5 V for the V_2O_5 films. Photopic transmittance was monitored in situ using a filtered silicon detector (International Light, Inc.) with output coupled to the computerized potentiostat/galvanostat. Transmittance and reflectance spectra between 300 and 2500 nm of complete, sealed, Sb–Cu/polymer gel electrolyte/V_2O_5 devices were recorded using a Perkin Elmer Lambda 19 UV/Vis/IR spectrophotometer.

2.2. Preparation of polymer gel electrolyte films and device assembly

The precursor solution contained 1 part by volume polyethylene glycol diacrylate (avg. molecular wt. 500), 10 parts 1 M $LiPF_6$ in PC/EC and AIBN initiator (1% mole ratio to the acrylate functional groups). Both electrodes were cycled 3 or 4 times in the liquid electrolyte before being coated with the gel electrolyte. The Sb–Cu film was in the mirror (delithiated) state and the V_2O_5 film was in the lithiated state when the gel electrolyte was applied. The precursor solution was applied to the electrodes using a doctor blade. The gel layers were exposed to 365 nm UV light for 15 min at room temperature in the He glove box to form uniform, transparent coatings. Complete devices were assembled by adding a small amount of additional precursor solution between the gel coated electrodes and UV curing from the V_2O_5 side for 30 min. The electrodes were bonded together very strongly by the crosslinked electrolyte after curing. The device was then sealed by applying low vapor pressure epoxy (Torr Seal, Varian Associates) to the edges. The active device area was 23 mm × 28 mm; the electrolyte thickness was 230 μm.

2.3. Electrolyte characterization

A 2 mm thick film of the electrolyte precursor solution was applied to a Teflon® plate and UV cured for 15 min at room temperature in the He glove box. A 5 mm diameter disc was cut from the gel film and loaded into a Rheometric SRA II solid analyzer. The elastic and loss moduli were measured over a frequency range of 1–100 rad/s at 25 °C. The conductivities of the liquid and gel electrolytes were measured in a special conductivity cell. The electrolyte precursor solution was sandwiched between a stainless-steel electrode and an ITO-coated glass electrode. The electrolyte thickness was defined by a 256 μm polypropylene spacer. The conductive area of the cell was 1.00 cm^2. The electrolyte was crosslinked in the cell by UV irradiation through the glass electrode. A Solartron™ SI1254 four-channel frequency response analyzer and a 1286 electrochemical interface were used to measure the impedance before and after gelation. To obtain a transmission spectrum of the polymer gel electrolyte, a 100 μm thick electrolyte precursor layer was sandwiched between two 1 mm thick plain glass plates and UV crosslinked.

3. Results and discussion

3.1. Electrolyte properties

The conductivity of the 1 M $LiPF_6$ in PC/EMC (1/1) electrolyte is 6.8 mS/cm [4]. Addition of polyethylene glycol diacrylate decreased the conductivity one order of magnitude to 0.673 mS/cm due to an increase in viscosity. Crosslinking, which significantly improved the mechanical properties of the electrolyte, reduced the conductivity only slightly, to 0.666 mS/cm (Fig. 1). The elastic modulus (E') of the crosslinked gel (Fig. 2) was 1.1×10^6 dyn/cm^2, with minimal frequency dependence.

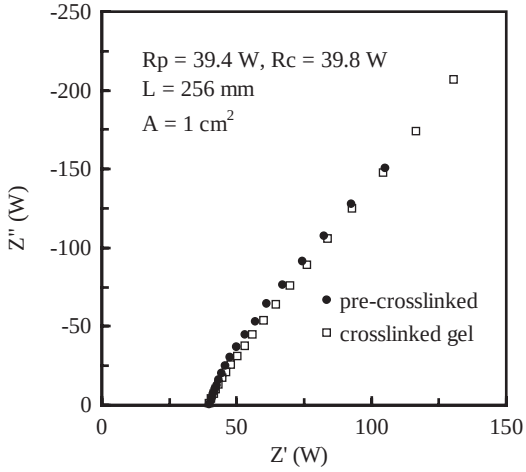

Fig. 1. Conductivity of the electrolytes before and after crosslinking.

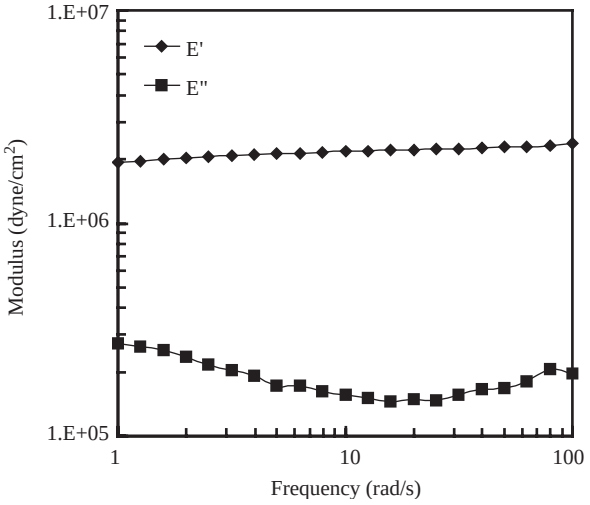

Fig. 2. The mechanical properties of the crosslinked electrolyte.

The loss modulus (E'') was an order of magnitude lower. These values are typical of a soft adhesive gel with good dimensional stability. The gel structure preserved the conductivity of the liquid electrolyte while maintaining the separator thickness and good contact with the electrodes. This also simplified device assembly and prevented electrolyte leakage. The transmission spectrum of the polymer, corrected for the contribution of the glass substrates, is shown in Fig. 3. The polymer is quite transparent in the visible and near IR, but has a weak absorption maximum at 1700 nm and becomes significantly absorbing above 2150 nm.

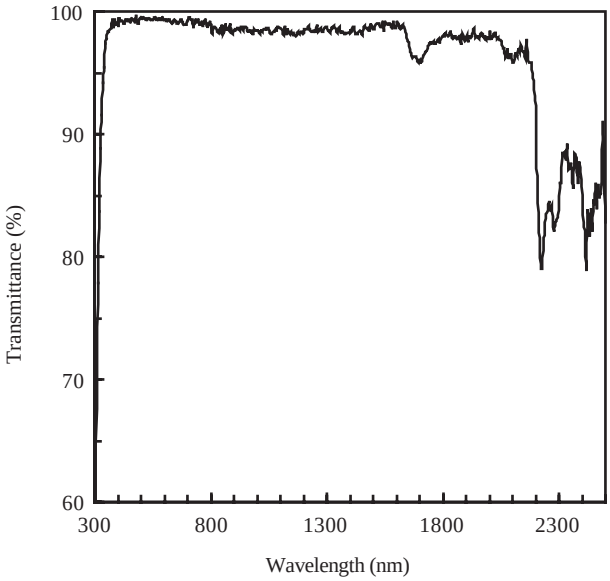

Fig. 3. The transmission spectrum of the crosslinked electrolyte, corrected for the glass substrates.

3.2. Electrode properties

The photopic transmittance and half-cell potential of the Sb–Cu electrode for the first three cycles are shown in Fig. 4(a). The features above 1.3 V during the initial lithiation are due to irreversible reduction of oxides formed in preparation and transfer to the glove box. The transmittance increased with lithiation from an initial value of 1.8% to a maximum of 32%. As shown in Fig. 4(b), this maximum always occurred after the reversal of the current flow in half cell and complete devices. The charge and discharge capacities were 64 μAh. The $Li_xV_2O_5$ electrode (Fig. 5) was strongly absorbing but only weakly electrochromic (41% T when lithiated, 48% T delithiated). The capacity stabilized after the second cycle at 80 μAh. Although a more transparent passive counter electrode can be prepared, since the primary purpose was to measure the optical properties of the Sb–Cu electrode outside the glove box, this electrode was deemed acceptable.

3.3. Device properties

The electrolyte remained highly transparent and free of bubbles and cracks even after several weeks of cycling and storage. No delamination or leakage occurred. Transmittance and mirror-side reflectance spectra of the complete device from 300 to 2500 nm recorded at the extremes of switching are shown in Fig. 6(a). The glass substrates absorb strongly below 340 nm, affecting both transmittance and reflectance. In the mirror state, the transmittance was low, with a broad maximum

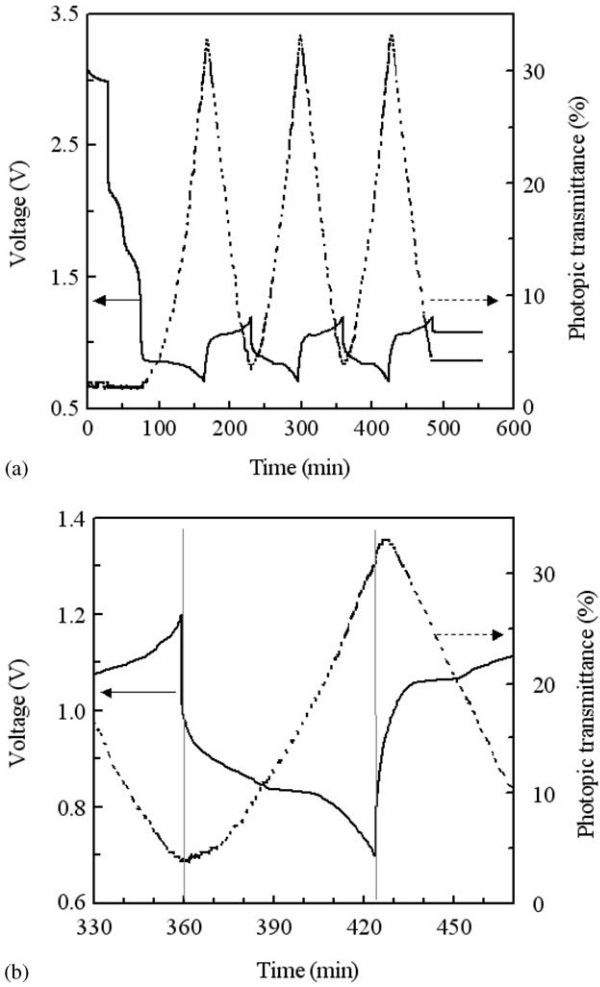

Fig. 4. (a) Voltage (vs. Li/Li^+) and photopic transmittance of Sb–Cu film during galvanostatic cycling at $10\,\mu A/cm^2$ in 1 M $LiPF_6$ in PC/EMC (1/1); (b) detail of third cycle. Vertical lines are visual aids.

at about 1100 nm. The reflectance increased with wavelength through the visible and into the near IR range to about 55% at 1200 nm, and held constant at longer wavelengths. In the transparent state, the transmittance increased rapidly beginning at 400 nm, reaching 30% at 1000 nm, then falling off at longer wavelengths due in part to the reflectance of the SnO_2:F coating behind the counter electrode. The reflectance decreased substantially on switching from the mirror to the transparent state, especially in the visible range. The transmission spectrum of the mirror electrode, obtained by correcting for absorption by the counter electrode and the polymer gel electrolyte, is shown in Fig. 6(b). The dynamic range in the visible region is about 10:1.

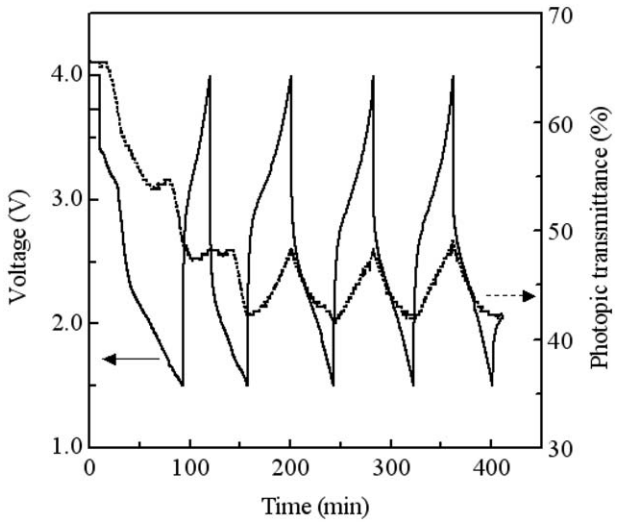

Fig. 5. Voltage (vs. Li/Li^+) and photopic transmittance of $Li_xV_2O_5$ electrode during galvanostatic cycling at $10\,\mu A/cm^2$ in 1 M $LiPF_6$ in PC/EMC (1/1).

It was found that potentiostatic cycling improved both the dynamic range of switching and cycling stability relative to galvanostatic cycling. The variation in photopic transmittance during the first 40 cycles at 1 mV/s between 1.0 and 3.0 V ($Li_xV_2O_5$ is positive) is shown in Fig. 7. The switching range increased gradually over the first 28 cycles and then began to decrease as the maximum transmittance achieved fell off. This is consistent with electronic disconnection of active areas, leaving them in the delithiated state. The cycling stability was significantly better than that observed in liquid electrolytes [2]. The cause of the minor increase in transmission following the reversal of current at the end of the bleaching step, which was also observed in both galvanostatic and potentiostatic modes is unknown.

4. Conclusions

A UV crosslinked gel polymer electrolyte was used to fabricate a self-contained switchable mirror based on transport of lithium ions between a sputtered Sb–Cu alloy mirror electrode and a sol–gel $Li_xV_2O_5$ counter electrode. The polymer provided excellent rigidity, adhesion, transparency, and conductivity. The stability of the mirror electrode was improved by the presence of the rigid polymer gel electrolyte. Further improvements in both stability and switching speed may be realized through the use of an inorganic solid-state electrolyte and a transparent current collector that is stable at low potentials. Efforts to protect transparent oxide conductors such as ITO or SnO_2:F by applying a thin barrier layer are in progress.

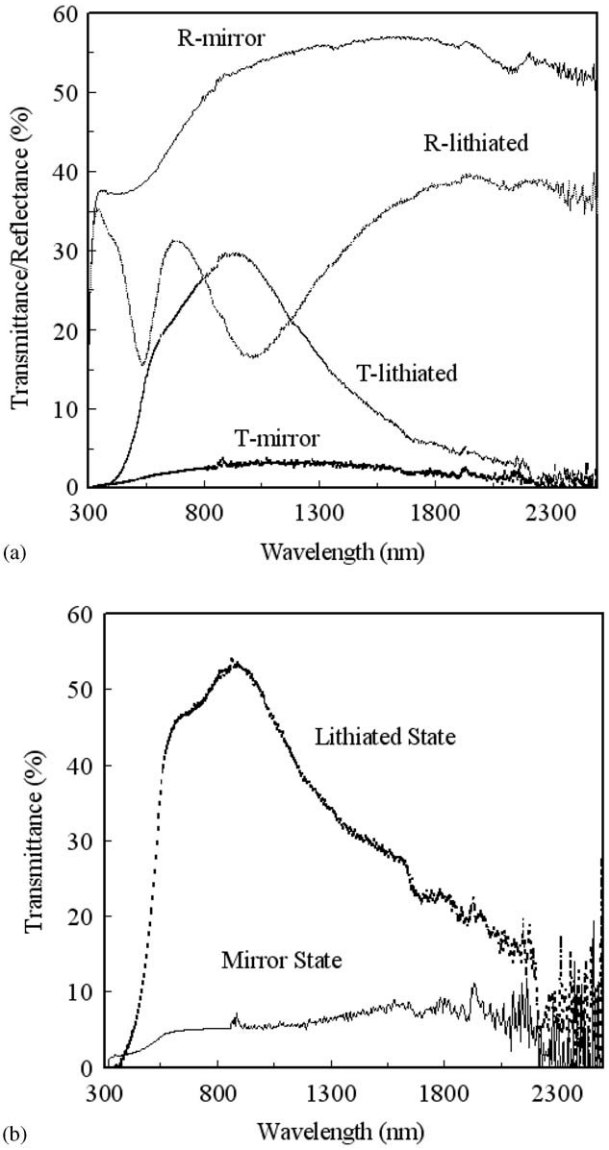

Fig. 6. (a) Transmittance and reflectance spectra of Sb–Cu/$Li_xV_2O_5$ device in mirror and transparent states; (b) transmittance spectrum of the Sb–Cu electrode without the contribution from the $Li_xV_2O_5$ electrode.

The counter electrode used in this device was strongly absorbing. Alternative compositions and processing techniques can be expected to produce higher quality electrodes which will be used to make switchable mirrors with considerably higher maximum transparency.

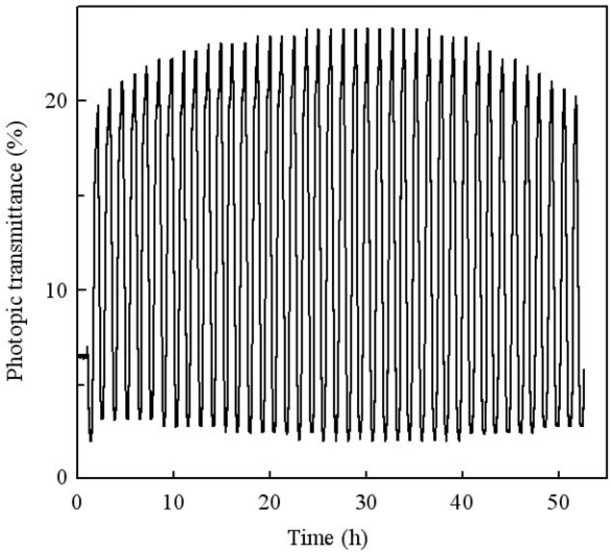

Fig. 7. Photopic transmittance versus time during potentiostatic charge and discharge of the device.

Acknowledgements

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